1,178,847

PATENT SPECIFICATION

NO DRAWINGS

1,178,847

Date of Application and filing Complete Specification: 6 March, 1967.

No. 10445/67.

Application made in Germany (No. C38496 IVc/39b) on 15 March, 1966.

Complete Specification Published: 21 Jan., 1970.

Index at acceptance: —C3 P(10C8B, 10C12B, 10C12X, 10C20A, 10C20D1, 10C20D2, 10D1A)

International Classification:—C 08 k 1/84

COMPLETE SPECIFICATION

Dry Granular Process and Product

We, CHEMISCHE WERKE MUNCHEN OTTO BARLOCHER G.m.b.H., a German Company of 16 D[illegible] mixed with the base resin

[illegible] the decomposition of polyvinyl chloride under the action of heat or light. Suitable stabilisers are inorganic lead compounds such as neutral or basic lead carbonates, sulphates and phosphites; organic lead compounds such as neutral or basic lead stearates and lead palmitates; organo-lead compounds such as diphenyl lead diacetate; neutral or basic lead salts of aromatic or polybasic carboxylic acids, such as salicylates, phthalates and maleates. Customary pulverulent metal soap stabilisers are cadmium soaps such as cadmium stearate and cadmium laurate, barium soaps, barium-cadmium soaps, calcium soaps, strontium soaps and zinc soaps. Rarely is one stabiliser used alone. It is usual to employ a plurality of stabilisers together, the properties of which complement one another. Similarly extensive conditions apply in the cases of other processing additives, and especially lubricants and fillers.

According to current practice, each of the various additives to be employed must be separately weighed and then homogeneously [illegible] the various additives to be mixed with the base resin. One proposal to that end has been for the additives supplier to put up, for supply to the plastics processor, packs of ready-mixed additive compositions or aggregates containing constituent additives (stabilisers, lubricants, fillers, etc.) in selected quantitative proportions such as are most favourable to meet the processor's requirements for producing particular types of plastics products. The mixes are packed in plastics bags in weighed amounts to suit the sizes of mixers used by plastic processors for preparing plastics blends for processing. The plastics bags are made of a thermoplastic, usually polyethylene, and are heat-sealed. The bags dissolve in the blend in the processor's mixer, and therefore need not be opened by the processor.

The specification of co-pending Patent Application No. 55019/66 (Serial No. 1178046) discloses a process by which uniform granulation of pulverulent substances which are insoluble or only slightly soluble in water may be achieved in the aqueous phase with the aid of certain organic compounds which are

1,178,847

PATENT SPECIFICATION

NO DRAWINGS

1,178,847

Date of Application and filing Complete Specification: 6 March, 1967.

No. 10445/67.

Application made in Germany (No. C38496 IVc/39b) on 15 March, 1966.

Complete Specification Published: 21 Jan., 1970.

Index at acceptance: —C3 P(10C8B, 10C12B, 10C12X, 10C20A, 10C20D1, 10C20D2, 10D1A)

International Classification:—C 08 k 1/84

COMPLETE SPECIFICATION

Dry Granular Process and Product

We, CHEMISCHE WERKE MUNCHEN OTTO BARLOCHER G.m.b.H., a German Company, of 16 Riesstrasse, 8 Munich 54, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The plastics processing industry utilises a large number of processing agents as additives to the plastics base materials to be processed. Such additives include, for example, plasticisers, lubricants, mould parting agents, fillers, antistatic agents, ultra-violet absorbers, expanding agents, dyestuffs and fire-retarding agents. Of particular importance for the processing of polyvinyl chloride are the pulverulent products utilised as stabilisers for suppressing or retarding the decomposition of polyvinyl chloride under the action of heat or light. Suitable stabilisers are inorganic lead compounds such as neutral or basic lead carbonates, sulphates and phosphites; organic lead compounds such as neutral or basic lead stearates and lead palmitates; organo-lead compounds such as diphenyl lead diacetate; neutral or basic lead salts of aromatic or polybasic carboxylic acids, such as salicylates, phthalates and maleates. Customary pulverulent metal soap stabilisers are cadmium soaps such as cadmium stearate and cadmium laurate, barium soaps, barium-cadmium soaps, calcium soaps, strontium soaps and zinc soaps. Rarely is one stabiliser used alone. It is usual to employ a plurality of stabilisers together, the properties of which complement one another. Similarly extensive conditions apply in the cases of other processing additives, and especially lubricants and fillers.

According to current practice, each of the various additives to be employed must be separately weighed and then homogeneously mixed with the base resin and the other additives, to obtain a dry blend of the constituents in desired proportions for subsequent processing. The greater the number of individual weighing operations, the greater will be the probability of errors in weighing and consequent lack of uniformity in the finished product, quite apart from considerations of time and cost consumed thereby. In the case of poisonous stabilisers, such as lead soaps for example, their fine powder form makes special safety precautions against poisoning necessary. Another disadvantage of products in fine powder form is their defective ability to flow freely, which prohibits continuous and controlled feed from storage silos.

Various attempts have, therefore, been made to simplify the proportioning of the various additives to be mixed with the base resin. One proposal to that end has been for the additives supplier to put up, for supply to the plastics processor, packs of ready-mixed additive compositions or aggregates containing constituent additives (stabilisers, lubricants, fillers, etc.) in selected quantitative proportions such as are most favourable to meet the processor's requirements for producing particular types of plastics products. The mixes are packed in plastics bags in weighed amounts to suit the sizes of mixers used by plastic processors for preparing plastics blends for processing. The plastics bags are made of a thermoplastic, usually polyethylene, and are heat-sealed. The bags dissolve in the blend in the processor's mixer, and therefore need not be opened by the processor.

The specification of co-pending Patent Application No. 55019/66 (Serial No. 1178046) discloses a process by which uniform granulation of pulverulent substances which are insoluble or only slightly soluble in water may be achieved in the aqueous phase with the aid of certain organic compounds which are

insoluble or only slightly soluble in water. Working in the aqueous phase, however, permits granulation of only some of the many additives usually employed for plastics processing. Moreover, the granular products so produced have to be dried. Furthermore, granulation of water-soluble substances is not possible by such process.

An object of the present invention is to provide a process whereby such additives for plastics processing can be granulated in the dry form.

The present invention accordingly consists in a process for the production of a granular product from pulverulent material selected from the group of additives for plastics processing, especially the processing of polyvinyl chloride, consisting of pulverulent inorganic and/or metal soap stabilisers, fillers, dyestuffs, antistatic agents and fire-retarding agents, which comprises mixing the selected pulverulent material or materials with a granulating agent consisting of at least one organic compound which has a melting point above 40°C, is solid and non-adhesive at room temperature, and has a molecular weight of above 150, preferably above 200, heating the mixture to melt the granulating agent while vigorously stirring the mixture, and then cooling the resultant hot mix to room temperature while under reduced stirring to form granules.

In the molten condition the granulating agent has a granulating action as a binder for the particles of the pulverulent material, and when in the solidified state again at room temperature acts as a parting agent to prevent the formed granules from sticking together.

Particularly suitable granulating agents are those compounds which are usually employed as lubricants in plastics processing. They generally contain a long chain hydrocarbon radical. Especially suitable are spermaceti or other esters derived from fatty alcohols or synthetic alcohols containing at least 6 carbon atoms and fatty acids, esters derived from fatty acids and polyhydric alcohols, and also partial esters such as glycerine monostearate, trimethylol propane distearate or pentaerythritol distearate, fatty alcohols, corresponding synthetic alcohols, fatty acids, corresponding synthetic acids, oxy- or halogen fatty acids.

In addition, paraffins, synthesis paraffins, montan waxes, improved montan waxes, hardened vegetable and animal oils such as hardened castor oil for example, ester waxes, fatty acid amides, fatty acid alkylolamides, fatty acid alkylol amine esters such as triethanol amine distearate, fatty amines, fatty ketones such as stearone, anhydrides of higher carboxylic acids, alkyl phenols, and long chain ethers such as distearyl ether or fatty alcohol polyglycol ether or alkylphenol polyglycol ether for example, are suitable as granulating agents. About 2—40%, preferably 7—15% is used, referred to the pulverulent material to be granulated.

Granulating agents which are very hard at room temperature and impart a brittle feel to the granules can be softened by means of suitable plasticisers. Hard granulating agents are, for example, the synthesis paraffins and the improved montan waxes having melting points of about 100°C, and ethylene-bis-stearamide having a melting point of about 135°C. However, waxes having lower melting points, such as carnauba wax for example, may also be hard and brittle at room temperature. The usual plasticisers such as mineral oils, chloroparaffins, epoxydised oils such as epoxydised soya bean oil, and also phthalate plasticisers such as dioctylphthalate, and phosphate plasticisers such as tricresylphosphate, are suitable for plasticising purposes.

The process according to the invention is particularly valuable for granulating inorganic substances such as metal oxides, hydroxides, basic hydroxides, carbonates, basic carbonates such as white lead for example, sulphates, basic sulphates such as tribasic lead sulphate for example, neutral or basic phosphites, and basic acetates, either singly or in mixtures, as well as metal soaps, particularly neutral or basic lead soaps, cadmium soaps, barium soaps, barium-cadmium soaps, calcium soaps, magnesium soaps, strontium soaps, tin soaps, alkali metal soaps, and zinc soaps. These compounds are customarily employed as stabilisers and fillers for halogen-containing polymers. The process is valuable also for granulating titanium dioxide and barytes.

The process according to the invention enables pulverulent additives used in plastics processing, and especially stabilisers and fillers, to be prepared in uniform granule form with the aid, as granulating agents, of the substances likewise, utilised as lubricant additives in the processing of plastics. Thereby, granules having their composition adapted to suit specific technical requirements may be produced. This represents a very considerable technical advance for the plastics processing industry, because the present invention now makes it possible for processing additive compositions, particularly stabilisers, fillers and lubricants, to be produced and utilised in the form of a single component, namely a uniform granular product the granules of which contain the required composition of additives. For the processor numerous weighing operations are saved and weighing errors and irregularities due to defective mixing are avoided.

A portion of the same plastics base material as that for which a processing additive composition is intended may be incorporated as a constituent in the granular composition in its process of production, preferably in amounts of 10% by weight of the composition. Thereby, the density of the granules is reduced and their affinity for the plastics base

material for which the additive composition is intended is increased, and thus the power of the composition to disperse in that plastics base material is improved.

A considerable technical improvement also lies in the granular form as such, because in contrast to products in fine powder form, the granular form is free-flowing, ensures freedom from dust, and has a virtually indefinite storage life. These qualities permit storage in silos and feeding at controlled rates of flow for accurately proportioned mixing with other constituents in a continuous process. The invention consequently opens up entirely new possibilities of continuous processing, for example for the continuous processing of polyvinyl chloride, which hitherto has been processed in batches.

In producing granular plastics processing additive compositions by the process according to the invention, the high melting point processing additives, such as inorganic stabilisers for polyvinyl chloride, pulverulent metal soaps, fillers, and possibly dyestuffs, antistatic agents, or fire-retarding agents, are introduced, together with the lubricants utilised here as granulating agents, into a high speed mixer provided with heating and cooling facilities. The mixing mechanism, is rotated at more than 1000 rpm for thoroughly mixing the constituents, and the mix is raised to a temperature above the melting point of the granulating agent. In the case of granulating agents having low melting points, for example tallow fatty alcohol having a melting point of about 48°C, this temperature is reached by frictional heat in the high-speed mixer, without need for heat to be applied. In the case of granulating agents having higher melting points, for example hardened castor oil having a melting point of 84°C, additional heating is applied. After the melting point of the granulating agent is exceeded so that the granulating agent is molten, the speed of rotation of the stirring mechanism is reduced to below 700 rpm, and if additional heating was previously applied, its supply is discontinued. The mix is cooled while the slow stirring is continued, until granules form. Depending on the speed of stirring, the temperature, and the granulating agent, smaller or larger granules having diameters of between 0.1 and 10 mm may be obtained. The melting points of the granulating agents lie between 40 and 150°C. The preferred granulation temperatures are between 45 and 55°C.

The following Examples illustrate the invention.

Example 1

5 kg of dibasic lead stearate, 5 kg of dibasic lead phosphite, 2 kg of neutral lead stearate, 15 kg of chalk coated with 2% calcium stearate, and 3 kg of cetyl palmitate are mixed at 1800 rpm in a mixer of 75 litre capacity, provided with heating and cooling facilities. After about 15 minutes mixing time the granulation temperature of about 50°C is reached by frictional heat without additional heating. Stirring is then continued at 600 rpm and cooling is applied. Granules having a mean diameter of 1 mm and a mean bulk density of 1160 grams per litre are obtained.

The granules are situable for single-component stabilisation of, for example, hard tubes of polyvinyl chloride.

Example 2

15 kg of dibasic lead sulphate, 15 kg of dibasic lead stearate, 4 kg of calcium stearate, 2 kg of stearic acid, and 2.5 kg of pentaerythrite distearate are mixed in a mixer having a capacity of 75 litres and heating and cooling facilities, the mixer working at 2000 rpm. Despite slight cooling with water, the granulation temperature of 55°C is reached by frictional heat after about 20 minutes mixing time. The mixture is stirred to coldness at 600 rpm with stronger cooling. Granules are obtained which have a mean diameter of 2 mm and a bulk density of 1050 grams per litre. These granules are used as stabiliser and lubricant in the processing of polyvinyl chloride in extruders.

WHAT WE CLAIM IS:—

1. A process for the production of a granular product from pulverulent material selected from the group of plastics processing additives consisting of pulverulent inorganic and/or metal soap stabiliers, fillers, dyestuffs, antistatic agents and fire-retarding agents, which comprises mixing the selected pulverulent material or materials with a granulating agent consisting of at least one organic compound which has a melting point above 40°C, is solid and non-adhesive at room temperature, and has a molecular weight of above 150, heating the mixture to melt the granulating agent while vigorously stirring the mixture, and then cooling the resultant hot mix to room temperature while under reduced stirring to form granules.

2. A process as defined in claim 1 wherein the granulating agent employed has a molecular weight of above 200.

3. A process as defined in claim 1 or 2 wherein the granulating agent employed is a lubricant used in processing plastics.

4. A process as defined in claim 1, 2 or 3 wherein the pulverulent material to be granulated is an additive or additives used in processing polyvinyl chloride, and the granulating agent is a lubricant used in processing polyvinyl chloride.

5. A process as defined in any one of the preceding claims wherein the granulating agent is selected from the group consisting of esters derived from fatty alcohols or synthetic

alcohols having at least 6 carbon atoms and fatty acids, esters derived from fatty acids and polyhydric alcohols, partial esters, fatty alcohols, corresponding synthetic alcohols, fatty acids, corresponding synthetic acids, oxy- or halogen fatty acids, paraffins, synthesis paraffins, montan waxes, improved montan waxes, hardened vegetable and animal oils, ester waves, fatty acid amides, fatty acid alkylolamides, fatty acid alkylol amine esters, fatty amines, fatty ketones, anhydrides of higher carboxylic acids, alkyl phenols, fatty ethers, fatty alcohol polyglycol ethers, and alkylphenol polyglycol ethers.

6. A process as defined in any one of the preceding claims wherein the granulating agent is utilised in a proportion in the range 2—40% by weight of the pulverulent material.

7. A process as defined in claim 6 wherein the proportion of granulating agent used is in the range 7—15% by weight of the pulverulent material.

8. A process as defined in any one of the preceding claims wherein the granulating agent used is an organic compound which is hard and brittle at room temperature, and a plasticiser therefor is incorporated in the mix to soften said compound in the granules formed.

9. A process as defined in claim 1 wherein the pulverulent material is selected from the group consisting of metal oxides, hydroxides, basic hydroxides, carbonates, basic carbonates, white lead, sulphates, basic sulphates, tribasic lead sulphate, neutral or basic phosphites, basic acetates, metal soaps, neutral or basic lead soaps, cadmium soaps, barium soaps, barium-cadmium soaps, calcium soaps, magnesium soaps, strontium soaps, tin soaps, alkali metal soaps and zinc soaps.

10. A process as defined in claim 1 wherein the pulverulent material is titanium dioxide.

11. A process as defined in claim 1 wherein the pulverulent material is barytes.

12. A process as defined in claim 1 wherein the granulating agent has a melting point between 40°C and 150°C.

13. A process as defined in claim 1 wherein the mixture is heated to a granulating temperature in the range 45—55°C.

14. A process as defined in claim 1 substantially as described in either one of the foregoing Examples.

15. A granulated product when produced by a process as defined in any one of the preceding claims.

16. A granular composition of matter comprising granules composed of a coherent mass of particles of a pulverulent material or materials selected from the group of plastics processing additives consisting of pulverulent inorganic and/or metal soap stabilisers, fillers, dyestuffs, antistatic agents and fire-retarding agents, bound with an organic binder which consists of an organic compound having a molecular weight of above 150 and a melting point above 40°C, the binder being solid and non-adhesive at room temperature.

For the Applicants:
BERNIER & BURRINGTON,
Chartered Patent Agents,
Chancery House,
53—64, Chancery Lane,
London, W.C.2.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1970.
Published by the Patent Office, 25, Southampton Buildings, London W.C.2, from which copies may be obtained.